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Abstract

Room-temperature ionic liquids are a class of nonmolecular ionic solvents with low melting points. Their properties have the potential to be especially useful as stationary phases in gas–liquid chromatography (GLC). A series of common ionic liquids were evaluated as GLC stationary phases. It was found that many of these ionic liquids suffer from low thermal stability and possess unfavorable retention behavior for some classes of molecules. Two new ionic liquids were engineered and synthesized to overcome these drawbacks. The two new ionic liquids (1-benzyl-3-methylimidazolium trifluoromethanesulfonate and 1-(4-methoxyphenyl)-3-methylimidazolium trifluoromethanesulfonate) are based on “bulky” imidazolium cations with trifluoromethanesulfonate anions. Their solvation characteristics were evaluated using the Abraham solvation parameter model and correlations made between the structure of the cation and the degree to which the ionic liquids retain certain analytes. The new ionic liquids have good thermal stability up to 260 °C, provide symmetrical peak shapes, and because of their broad range of solvation-type interactions, exhibit dual-nature selectivity behavior. In addition, the ionic liquid stationary phases provided different retention behavior for many analytes compared to a commercial methylphenyl polysiloxane GLC stationary phase. This difference in selectivity is due to the unique solvation characteristics of the ionic liquids and makes them very useful as dual-nature GLC stationary phases.

Keywords

Ionic liquids, Ionic conduction, melting, solvents, gas chromatography, polysiloxane, analytic method, drug stability, electrochemistry, matrix assisted laser desorption ionization time of flight mass spectrometry

Disciplines

Analytical Chemistry | Chemistry

Comments

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High-Stability Ionic Liquids. A New Class of Stationary Phases for Gas Chromatography

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Room-temperature ionic liquids are a class of non-molecular ionic solvents with low melting points. Their properties have the potential to be especially useful as stationary phases in gas–liquid chromatography (GLC). A series of common ionic liquids were evaluated as GLC stationary phases. It was found that many of these ionic liquids suffer from low thermal stability and possess unfavorable retention behavior for some classes of molecules. Two new ionic liquids were engineered and synthesized to overcome these drawbacks. The two new ionic liquids (1-benzyl-3-methylimidazolium trifluoromethanesulfonate and 1-(4-methoxyphenyl)-3-methylimidazolium trifluoromethanesulfonate) are based on “bulky” imidazolium cations with trifluoromethanesulfonate anions. Their solvation characteristics were evaluated using the Abraham solvation parameter model and correlations made between the structure of the cation and the degree to which the ionic liquids retain certain analytes. The new ionic liquids have good thermal stability up to 260 °C, provide symmetrical peak shapes, and because of their broad range of solvation-type interactions, exhibit dual-nature selectivity behavior. In addition, the ionic liquid stationary phases provided different retention behavior for many analytes compared to a commercial methylphenyl polysiloxane GLC stationary phase. This difference in selectivity is due to the unique solvation characteristics of the ionic liquids and makes them very useful as dual-nature GLC stationary phases.

Room-temperature ionic liquids (RTILs), formally known as molten salts, are a class of nonmolecular ionic solvents with low melting points. Most common RTILs are composed of unsymmetrically substituted nitrogen-containing cations (e.g., based on imidazole, pyrrole, or pyridine) with inorganic anions (e.g., Cl⁻, PF₆⁻, BF₄⁻, etc.). Ionic liquids are of interest due to their unique physical and chemical properties. These liquid salts have little measurable vapor pressure at room temperature, can be custom synthesized to be water-miscible or water-immiscible, and are capable of undergoing multiple solvation interactions with many types of molecules. The uses and properties of RTILs have been the focus of many recent scientific investigations.^{1–30} Their uses

include novel solvent systems in organic synthesis,^{1–9} enzyme-catalyzed reactions,¹⁰ electrochemical studies,^{11–14} electrolyte materials for double-layer capacitors,¹⁵ dye-sensitized solar cells,¹⁶ liquid–liquid extraction,^{17–20} ultralow volatility liquid matrices for matrix-assisted laser desorption/ionization mass spectrometry,^{21,22} run buffer additives in capillary electrophoresis,^{23,24} and stationary phases in gas–liquid chromatography (GLC).^{25–30}

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It has been demonstrated that simple polarity parameters do not adequately describe the nature of RTILs or the physical–chemical behavior of compounds dissolved in them.^{25,27} The interactions between ionic liquids and dissolved molecules can be much more varied and complex than what is possible with simple molecular solvent systems.

Recently, we reported that RTILs can be characterized by five different interaction parameters and that these parameters can be used to explain the solution and reaction behavior of compounds dissolved in RTILs.²⁷ It was shown that the unique combination of cations and anions affected the RTIL's ability to undergo multiple solvation interactions with other molecules. Specifically, the anion appears to have a direct influence on the hydrogen bond basicity and dipolarity of the RTIL while the cation, depending on its structure, can influence the ability of the RTIL to interact via nonbonding and π electrons. The nature of both the cations and anions influences dispersion forces and hydrogen bond acidity interactions.

The first report on the use of an organic salt as a stationary phase for gas chromatography was by Barber et al.³¹ The retention properties of a wide range of solutes on stearate salts of the bivalent metals manganese, cobalt, nickel, copper, and zinc were investigated. However, many of these early fatty acid–salt stationary phases suffered from limited liquid ranges and poor chromatographic efficiencies.

Gordon et al. investigated the stationary-phase properties of tetra-*n*-pentylammonium picrate and bromide and of tetra-*n*-hexylammonium nitrate.³² Despite the fact that the liquid range, thermal stability, and column efficiencies were low, these stationary phases exhibited selective interactions between polar and hydrogen bond-forming solutes. Poole and co-workers later examined the stationary-phase characteristics of the organic molten salt ethylammonium nitrate.³³ They found this salt had a usable temperature range from <20 to 120 °C and retained compounds containing dipolar and hydrogen-bonding functional groups. However, this stationary phase showed no significant retention of *n*-hydrocarbons. The chromatographic performance and selectivity of the organic liquid salt ethylpyridinium bromide was also examined by the same group.³⁴ This stationary phase was able to separate a wide range of organic compounds, except for alkylamines and phenols. However, the column had a maximum operating temperature of 160 °C and produced separations with low efficiency below 110 °C.

In this work, we show that specifically engineered RTILs are particularly useful in GLC as they possess many of the requirements necessary for a good liquid stationary phase including high viscosity, high thermal stability, high wetting ability on fused-silica capillary tubing producing efficient separations, and very low effective vapor pressure. In addition, RTILs can be custom synthesized to be more viscous, possess a higher thermal stability range, or provide specific solute–RTIL interactions simply by changing the nature of the cation or anion.

Since our initial paper demonstrating imidazolium-based RTILs as stationary phases in GLC,²⁵ we were specifically interested in

their “dual-nature” behavior. That is, because ionic liquids are capable of solvating a large range of both polar and nonpolar molecules, they are capable of separating polar compounds as if they are polar stationary phases and nonpolar compounds as if they are nonpolar stationary phases. The dual-nature behavior refers to the selectivity of the ILs, that is, their ability to discriminate between similar molecules. In this work, we further investigate this dual-nature behavior by examining new bulky ILs that can be used at higher temperatures, often comparable to commercial GLC phases. In addition, we show that these stationary phases can have unusual selectivities and their dual-nature behavior can be exploited to separate complex mixtures of molecules of very different polarities. Given their unique selectivities, ionic liquid-based stationary phases may be particularly useful as one of the columns in GC \times GC applications.^{35,36}

EXPERIMENTAL SECTION

Materials. 1-Benzylimidazole, 1-methylimidazole, 1-chlorobutane, 1-chlorohexane, 1-(4-methoxyphenyl)-1*H*-imidazole, methyl trifluoromethanesulfonate (methyl triflate), hexafluorophosphoric acid, lithium trifluoromethanesulfonimide, dichloromethane, and all test solutes were purchased from Aldrich (Milwaukee, WI). Hexafluorophosphoric acid is a corrosive, toxic solution and must be handled with care. Analytical standards of chlorinated pesticides and polycyclic aromatic hydrocarbons (PAHs) were purchased from PolyScience Corp. (Niles, IL) and Supelco (Belefonte, PA), respectively.

Polychlorinated biphenyl (PCB) standards were provided by Dr. Shubhen Kapila (Rolla, MO). All sulfoxide samples were prepared according to previously published procedures.³⁷ Untreated fused-silica capillary (0.25-mm i.d.) was purchased from Supelco. DB-17 column (50% phenyl/50% methyl silicone, 10 m \times 0.25 mm i.d., film thickness 0.15 μ m) was purchased from J & W Scientific (Folsom, CA).

Methods. The synthesis of 1-butyl-3-methylimidazolium chloride (BMIM-Cl), 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM-PF₆), 1-butyl-3-methylimidazolium triflate (BMIM-TfO), and 1-butyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide (BMIM-NTf₂) are described elsewhere.^{4,5,25,27}

Briefly, BMIM-Cl was synthesized and used as the precursor salt to produce BMIM-PF₆ (using HPF₆), and BMIM-NTf₂ (using LiN(CF₃SO₂)₂). BMIM-TfO was produced by reacting equimolar amounts of 1-butylimidazole with methyl trifluoromethanesulfonate under argon. In each case, the resulting ionic liquid was thoroughly washed, and the washings were treated with silver nitrate until no silver chloride precipitate was observed. It is well known that residual chloride impurities can have a large effect on the physical properties of the RTILs, especially the hydrogen bond basicity.^{27,38} Therefore, purity was examined using ion chromatography and residual chloride ion concentration was less than 1 ppm.

1-Benzyl-3-methylimidazolium triflate (BeMIM-TfO) and 1-(4-methoxyphenyl)imidazolium triflate (MPMIM-TfO) were synthesized by reacting melted 1-benzylimidazole (0.06 mol) and 1-(4-

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methoxyphenyl)imidazole (0.06 mol) with equimolar amounts of methyl triflate added dropwise over a period of 2 h under argon to prevent methyl triflate hydrolysis. The resulting viscous liquids were washed with three 20-mL portions of ethyl acetate and evaporated under vacuum. 1-Benzyl-3-hexylimidazolium hexafluorophosphate (BeHIM-PF₆) was synthesized through the chloride salt by refluxing 1-benzylimidazole (0.04 mol) and 1-chlorohexane (0.04 mol) at 120 °C for 72 h. The very viscous RTIL was dissolved in ~150 mL of water, hexafluorophosphoric acid (0.07 mol) was slowly added, and the solution stirred overnight.

The lower liquid portion was washed with water until the washings were no longer acidic. The recovered ionic liquid (~83% yield) was then heated under vacuum at 80 °C to eliminate excess water. All synthesized compounds were characterized using HPLC-MS.

All capillary columns were coated by the static coating method at 40 °C using 0.24% (w/v) of the RTIL stationary phase dissolved in dichloromethane. Following the coating process, the coated columns were flushed with dry helium gas overnight and then conditioned from 30 to 220 °C at 0.5 °C/min. Column efficiency was tested using naphthalene at 100 °C. All columns had between 1900 and 2300 plates/m. To ensure that the coated layer was not altered during the chromatographic separations, the efficiency and retention factors of various solute molecules were monitored daily.

Test solutes used to determine interaction parameters were dissolved in dichloromethane. A Hewlett-Packard model 6890 gas chromatograph and a Hewlett-Packard 6890 series integrator were used for all separations. Split injection and flame ionization detection were utilized with injection and detection temperatures of 250 °C.

Helium was used as the carrier gas with a column inlet pressure of 3.1 psi and flow rate of 1.0 mL/min. Methane was used to determine the dead volume of the column.

Multiple linear regression analysis and statistical calculations were performed using the program Analyze-it (Microsoft).

RESULTS AND DISCUSSION

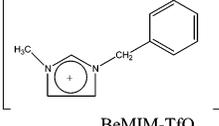
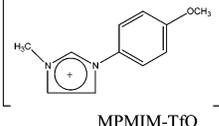
Newly proposed stationary phases for gas chromatography are nearly always characterized by their Rohrschneider-McReynolds constants. However, the Abraham solvation parameter model can also be used to describe the multiple solvation interactions between probe molecules and the stationary phase by using an inverse GLC approach.^{39,40} This model has been used recently to characterize many traditional RTILs.²⁷ Briefly, the solute descriptors (R_2 , π_2^H , α_2^H , β_2^H , $\log L^{16}$) from the solvation model of Abraham (eq 1) are obtained from the literature for many probe

$$\log k = c + rR_2 + s\pi_2^H + a\alpha_2^H + b\beta_2^H + l\log L^{16} \quad (1)$$

molecules containing a variety of functional groups.³⁹

The retention factor is determined chromatographically. The solute descriptors and retention factors are subjected to multiple linear regression analysis to obtain the interaction parameter coefficients (r , s , a , b , l), which ultimately characterize the stationary phase: r is the ability of the RTIL to interact with π and n electrons of the solute, s is a measure of the dipolarity/

Table 1. Structure, Molecular Weight, Melting Point, and Density of Newly Synthesized Ionic Liquids Proposed as Stationary Phases for Gas Chromatography

IL structure	MW	mp (°C)	density (g/cm ³)
	322.30	27	1.30 ^a
	338.30	45	1.32 ^b

^a Density measured at 30 °C. ^b Density measured at 50 °C.

polarizability of the RTIL, a defines the RTIL hydrogen bond basicity, b is a measure of the hydrogen bond acidity, and l refers to the ability of the RTIL to separate adjacent members of a homologous series.⁴¹

Two newly synthesized ionic liquids (ILs) are proposed as GLC stationary phases capable of providing unique selectivity for wide variety of molecules (see Table 1).

These two ILs have been designed to provide efficient separations and low column bleed.

Table 2 lists the five interaction parameters obtained from the aforementioned solvation model for five, well-known RTILs and three new ILs that contain bulky aromatic moieties on the cation and have triflate anions. Previously, we demonstrated that the anion has a direct influence on the hydrogen bond basicity (a term).²⁷ Since two of the new ILs have triflate anions, their hydrogen bond basicities should be very similar to those of previously evaluated triflate-containing RTILs. Indeed, it is observed that their hydrogen bond basicities (the a terms) are very similar to each other as well as the previously evaluated BMIM-TfO RTIL (see Table 2). Likewise, the PF₆⁻ salts evaluated in this study have similar a terms. Therefore, without knowing anything about a RTIL, it often is possible to identify the anion simply by using the solvation model and knowing ranges of hydrogen bond basicity values for various RTILs. Another interesting characteristic of the two new triflate ILs (BeMIM-TfO and MPMIM-TfO) is the difference in their hydrogen bond acidity (b) and their ability to interact via π and nonbonding electrons (i.e., their r -interaction parameters). BeMIM-TfO possesses considerably lower b and r interaction parameters compared to the MPMIM-TfO ionic liquid. An explanation for this behavior relates to the position of the phenyl ring with respect to the imidazolium ring. In the case of BeMIM-TfO, the phenyl ring is separated from the imidazolium ring by a methylene group, which effectively insulates the weakly activating phenyl ring from the imidazolium ring.

However, with the MPMIM-TfO ionic liquid, the phenyl group is connected directly to the imidazolium ring and also contains the activating methoxy group in the para position.

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Table 2. Comparison of Interaction Parameters Obtained Using the Solvation Parameter Model

compound ^a	interaction parameter ^b					no. of probes, <i>n</i>	corr coeff, <i>R</i> ²
	<i>r</i>	<i>s</i>	<i>a</i>	<i>b</i>	<i>l</i>		
MPMIM-TfO							
70 °C	0.540	2.055	2.826	0.585	0.403	29	0.98
100 °C	0.276	2.049	2.634	0.157	0.380	25	0.99
BeMIM-TfO							
70 °C	0.207	1.800	2.621	0.182	0.483	33	0.98
100 °C	0	1.695	2.414	0	0.468	25	0.98
BeHIM-PF ₆							
70 °C	0.073	1.913	1.813	0.131	0.536	32	0.99
100 °C	0.082	1.761	1.564	0.067	0.458	30	0.99
BMIM-Cl ^c							
70 °C	0.291	2.007	5.230	-0.320	0.445	22	0.98
100 °C	0.408	1.826	4.860	-0.121	0.392	23	0.98
BMIM-TfO ^c							
70 °C	0	1.727	2.713	0	0.516	31	0.99
100 °C	0	1.386	2.353	0	0.485	32	0.96
BMIM-NTf ₂ ^c							
70 °C	0	1.671	1.752	0.378	0.557	35	0.99
100 °C	0	1.596	1.551	0.235	0.487	32	0.98
BMIM-PF ₆ ^c							
70 °C	0	1.695	1.579	0	0.515	33	0.99
100 °C	0	1.540	1.369	0	0.439	32	0.98
BMIM-SbF ₆ ^c							
70 °C	0	1.808	2.704	-0.365	0.509	31	0.97
100 °C	0	1.659	2.276	-0.332	0.456	30	0.95

^a For abbreviations, see text. ^b Parameters: *r*, ability of stationary phase to interact via nonbonding and π electrons of solute molecule; *s*, stationary-phase dipolarity; *a*, stationary-phase hydrogen bond basicity; *b*, stationary-phase hydrogen bond acidity; *l*, stationary-phase dispersion forces. ^c The interaction parameter values were obtained from ref 27.

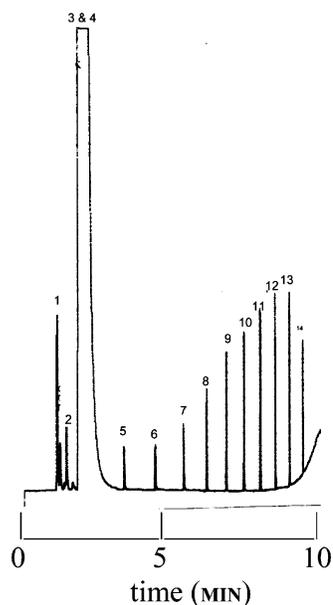


Figure 1. Separation of homologous series alkanes on a 15-m BMIM-SbF₆ column. 1, pentane; 2, hexane; 3 and 4, CH₂Cl₂ and heptane; 5, octane; 6, nonane; 7, decane; 8, undecane; 9, dodecane; 10, tridecane; 11, tetradecane; 12, pentadecane; 13, hexadecane; 14, heptadecane. Conditions: initial, 30 °C for 3 min; ramp, 15 °C/min to 170 °C.

This likely withdraws electrons from the imidazolium ring to the phenyl ring making it more π basic and able to interact via nonbonding and π electrons with solute molecules while also making the three imidazole hydrogen atoms (especially the hydrogen in position 2) more acidic.

Figure 1 and Figure 1 in Supporting Information show GLC chromatograms obtained using common RTIL stationary phases (BMIM-SbF₆ and BMIM-TfO). The chromatograms portray many of the ideal characteristics seen with RTIL stationary phases. For example, they are able to separate both polar and nonpolar molecules quite well. In addition to this dual-nature behavior, the separations can be achieved with high efficiency for most molecules. However, the three main drawbacks of conventional RTILs when used as stationary phases are the following: the maximum operating temperatures that can be employed, the peak efficiencies of certain analytes (i.e., solutes that are proton donors, specifically alcohols and acids) are not good, and the fact that a few analytes are tenaciously retained (some acids and bases). Clearly, RTILs have the potential to be the most broadly selective GLC stationary phases, but a way must be found to circumvent their shortcomings.

Optimal Cation/Anion Combinations for Low Bleed and High Thermal Stability. Although column bleed is observed for all GLC stationary phases, most of the traditional RTILs possess column bleed temperatures below 200 °C. In some cases, this is the result of decomposition, but in others, it is from slight volatilization of the RTIL.

Figure 1 shows an ideal separation of *n*-alkanes on the BMIM-SbF₆ stationary phase.

However, at higher temperatures (at ~8.5 min), the RTIL begins to bleed, resulting in a noticeable rising baseline. Figure 2 shows the “bleed temperatures” obtained for five traditional RTILs and the three new “bulky” ILs. It is apparent from this plot that each RTIL has a unique bleed temperature. Although the thermal stability of ionic liquids is dependent on the cation/anion combination, thermal stability generally increases with increased

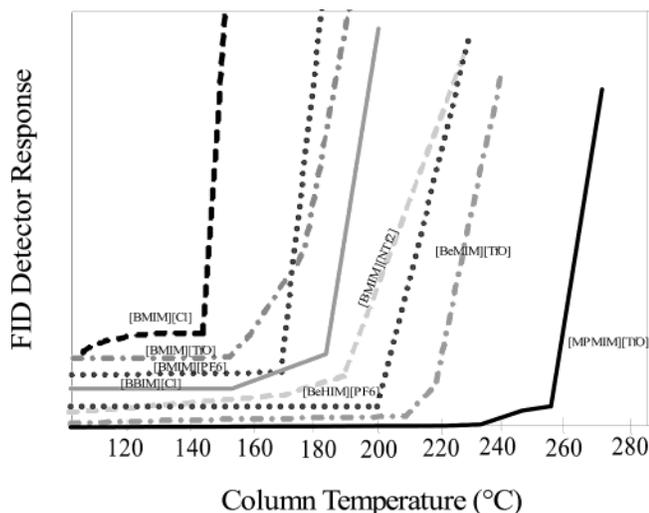


Figure 2. Thermal bleed diagram illustrating the volatilization temperatures of various traditional RTILs and the two new bulky-type ILs: BMIM, 1,3-dibutylimidazolium, (BBIM), BeMIM, BeHIM, MPMIM, BMIM-Cl (~145 °C), BMIM-TfO (~175 °C), BMIM-PF₆ (~170 °C), BBIM-Cl (~180 °C), BMIM-NTf₂ (~185 °C), BeHIM-PF₆ (~200 °C), BeMIM-TfO (~220 °C), and MPMIM-TfO (~250 °C).

alkyl substitution, as long as linear alkyl groups are used.⁴² This anomaly can be observed in Figure 2 when the thermal bleed temperatures of BMIM-Cl and 1,3-dibutylimidazolium chloride (BBIM-Cl) are compared where the symmetrical IL increases the bleed temperature by nearly 35 °C. In general, the relative thermal stabilities of ILs are affected by their anions as follows: PF₆⁻ > NTf₂⁻ ≈ BF₄⁻ > AsF₆⁻ > I⁻, Br⁻, Cl⁻.⁴²

In choosing the appropriate cation, RTILs with bulky substituents on both the 1 and 3 positions of the imidazolium ring were examined in hopes of increasing the volatilization temperature of the RTIL. According to Figure 2, 1,3-dibutylimidazolium chloride began to bleed near 180 °C. Interestingly, BeHIM-PF₆, although made bulkier with the addition of an alkyl group instead of a methyl group, volatilized at nearly 200 °C. However, in synthesizing BeMIM-TfO and MPMIM-TfO, the volatilization temperature increased to nearly 220 and 260 °C, respectively. Therefore, these two ionic compounds were chosen and their retention behaviors examined for a variety of different molecules.

While investigating the performance of each stationary phase, it was observed that the anion also plays a crucial role in the efficiency of the chromatographic separations, especially when separating molecules capable of donating protons. Table 3 lists the peak asymmetry factors⁴³ for *p*-cresol on six RTIL stationary phases. As can be seen from this table, the nature of the anion (the cation is kept constant) determines the extent to which tailing is observed on the RTIL phases. RTILs with triflate anions generally gave the most efficient separations while those containing the bis[(trifluoromethyl)sulfonyl] imide (NTf₂) anions gave the poorest efficiency. An explanation for this behavior may be due to the hydrogen bonding of the solute molecule to the delocalized negative charge on the weakly basic NTf₂ anion.²⁷ Table 4 further illustrates how the anion influences the retention

Table 3. Peak Asymmetry Factors for *p*-Cresol at 70 °C on Six RTIL GLC Stationary Phases

RTIL	peak asymmetry factor
BMIM-TfO	1.08
BMIM-SbF ₆	1.35
BMIM-BF ₄	1.41
BMIM-PF ₆	1.31
BMIM-Cl	1.45
BMIM-NTf ₂	2.50

of specific analytes. BMIM-Cl tenaciously retains analytes capable of proton donating (e.g., acids, alcohols) while BMIM-PF₆ shows less hydrogen bond basicity behavior but still strongly retains straight-chained hydrocarbons. Indeed, the choice of the anion not only influences the overall thermal stability but also plays a dominant role in how analyte molecules retain on the stationary phase. Therefore, ILs based on the triflate anion were chosen due to their ability to provide the most efficient separations of a wide variety of molecules, particularly carboxylic acids and alcohols.

Evaluation of Retention and Dual-Nature Behavior. Retention factors for a variety of different molecules are displayed in Table 4 and in the Supporting Information. The effects of different cations and anions on solute retention are shown for the BeMIM-TfO and MPMIM-TfO stationary phases and the older BMIM-Cl and BMIM-PF₆ stationary phases. It is quite apparent that, of the four ILs, the BMIM-Cl phase has unique retention behavior. For example, many molecules (e.g., phenol, *p*-cresol, and 1-octanol) capable of donating a proton did not elute from this column due to the phase's high hydrogen basicity (see Table 2 for the relevant interaction parameters). Additionally, many molecules eluted with the dead volume. The BMIM-PF₆ stationary phase, which possesses the lowest hydrogen bond basicity of the evaluated phases, retains proton-donating molecules to a lesser extent than the BMIM-Cl, BeMIM-TfO, and MPMIM-TfO stationary phases. However, this stationary phase does show enhanced selectivity for straight-chained hydrocarbons in retaining these compounds much more than the other three ILs. An explanation for this behavior lies with the interaction parameter, *I*, which measures dispersion forces and is highest for this stationary phase and lowest for the MPMIM-TfO phase at 70 °C (see Table 2). It is obvious that the BMIM-Cl stationary phase, due to its very high retention of alcohols and carboxylic acids and relatively low thermal stability (see Figure 2), would not be a practical stationary phase. The BMIM-PF₆ stationary phase retains acids and carboxylic acids to a lesser extent but also suffers from relatively low thermal stability and relatively high peak asymmetry factors (Table 3). Therefore, the focus of the remainder of this paper will be on the BeMIM-TfO and MPMIM-TfO stationary phases, which have been engineered to avoid the aforementioned disadvantages of the BMIM-Cl and BMIM-PF₆ stationary phases (see Supporting Information).

A chromatogram displaying the separation of a mixture of polar and nonpolar molecules on the BeMIM-TfO stationary phase is shown in Figure 3A. Nonpolar molecules generally eluted faster than polar molecules while molecules capable of donating protons (e.g., octanoic acid) were more strongly retained. The separation selectivity and efficiency of alkanes was excellent, whereas polar molecules exhibited broader peaks. This is likely due to the fact

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Table 4. Effect of Different Cations and Anions on the Retention Factors of Various Solute Molecules

compounds	[BeMIM-TfO]	[MPMIM-TfO]	[BMIM-Cl]	[BMIM-PF ₆]
(A) Paraffins				
<i>n</i> -octane ^a	0.28	0.06	<i>e</i>	0.52
<i>n</i> -nonane ^a	0.70	0.45	0.22	1.3
<i>n</i> -decane ^a	1.6	1.0	0.84	3.0
<i>n</i> -octacosane ^d	26.6	16.9	<i>g</i>	<i>g</i>
<i>n</i> -triacontane ^d	53.1	33.5	<i>g</i>	<i>g</i>
(B) Substituted Alkanes				
1-nitropropane ^a	1.3	1.0	2.1	2.7
1-chlorohexane ^a	0.57	<i>e</i>	<i>e</i>	1.4
propionitrile ^a	0.49	0.41	<i>e</i>	1.1
(C) Aromatics^a				
1,2-dichlorobenzene ^a	3.5	2.2	8.1	7.7
<i>o</i> -xylene ^a	1.1	0.53	1.3	2.6
<i>p</i> -xylene ^a	0.85	0.36	1.1	2.1
<i>m</i> -xylene ^a	0.86	0.37	1.0	2.1
nitrobenzene ^a	19.6	19.3	42.5	35.8
toluene ^a	0.43	0.2	<i>e</i>	1.1
benzene ^a	0.20	<i>e</i>	<i>e</i>	0.51
benzotrile ^a	10.1	9.5	24.1	20.3
naphthalene ^a	17.9	15.7	34.1	36.8
(D) Alcohols				
<i>p</i> -cresol ^a	247.8	248.5	<i>f</i>	96.1
phenol ^a	165.6	158.3	<i>f</i>	59.8
cyclohexanol ^a	4.2	2.9	<i>f</i>	4.1
butanol ^a	0.75	0.60	10.9	0.77
1-octanol ^a	8.4	5.5	73.1	10.0
2-propanol ^a	0.20	0.18	2.6	0.81
1,2-propanediol ^b	3.0	2.8	<i>f</i>	4.3
1,3-propanediol ^b	8.7	8.1	<i>f</i>	9.6
1,2-pentanediol ^b	5.5	5.0	<i>f</i>	6.7
(E) Aldehydes, Amides, Esters, Ketones				
octylaldehyde ^a	2.5	1.1	2.4	5.3
valeraldehyde ^a	0.35	0.23	8.2	0.76
<i>N,N</i> -dimethylformamide ^a	9.0	8.1	7.5	16.5
benzaldehyde ^a	7.6	7.2	16.6	15.1
acetophenone ^a	17.0	16.3	25.9	33.8
methyl caproate ^a	1.3	0.54	1.2	2.8
ethyl acetate ^a	<i>e</i>	<i>e</i>	0.17	0.38
cyclohexanone ^a	3.1	2.1	2.9	5.4
2-pentanone ^a	0.41	0.27	<i>e</i>	0.86
(F) Amines				
pyridine ^a	3.8	3.9	1.8	2.4
aniline ^a	46.6	41.1	<i>f</i>	52.6
2-chloroaniline ^a	58.5	49.3	<i>f</i>	70.8
(G) Carboxylic Acids				
acetic acid ^a	6.5	5.5	<i>f</i>	2.1
octanoic acid ^b	7.9	1.7	<i>f</i>	0.7
2-chloropropionic acid ^b	13.8	12.5	<i>f</i>	9.3
(H) Miscellaneous Compounds				
pyrrole ^a	7.4	6.7	115.3	7.9
ethyl phenyl ether ^a	3.0	1.9	3.9	6.5
dioxane ^a	0.62	0.46	<i>e</i>	1.2
<i>p</i> -trifluoromethyl methylphenyl sulfoxide ^c	3.2	3.4	<i>g</i>	<i>g</i>
<i>m</i> -bromo methylphenyl sulfoxide ^c	14.8	16.5	<i>g</i>	<i>g</i>
2,2',4,4'-tetrachlorobiphenyl ^c	6.0	5.4	<i>g</i>	<i>g</i>
2,2',4,4',6,6'-hexachlorobiphenyl ^c	8.1	6.6	<i>g</i>	<i>g</i>
pyrene ^d	12.2	17.7	<i>g</i>	<i>g</i>
1,2-benzanthracene ^d	10.2	26.7	<i>g</i>	<i>g</i>
heptachlor ^d	1.7	1.3	<i>g</i>	<i>g</i>
DDT ^d	12.3	11.0	<i>g</i>	<i>g</i>

^a 70 °C. ^b 120 °C. ^c 170 °C. ^d 200 °C. *e* Indicates solute eluted with dead volume. *f* Indicates solute did not elute under given conditions. *g* Indicates RTIL stationary phase could not be used at specific temperature due to volatilization of the IL.

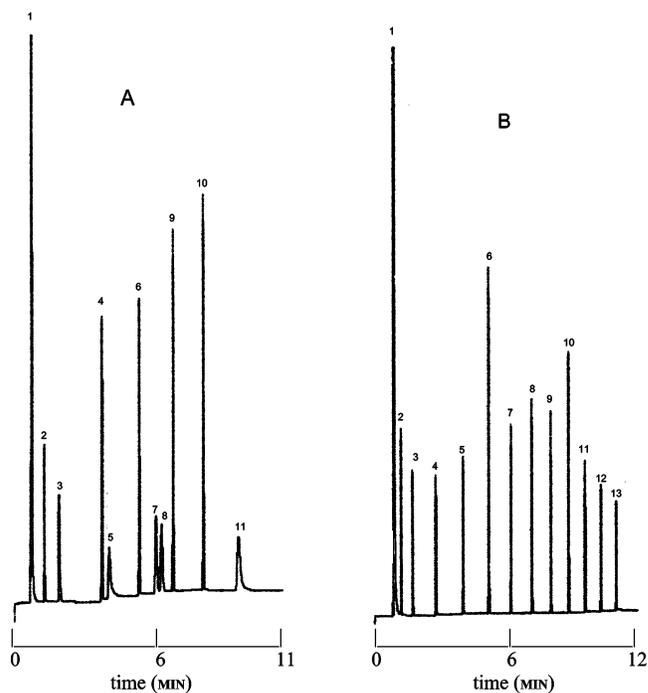


Figure 3. (A) Separation of polar/nonpolar mixture: 1, CH₂Cl₂; 2, methyl caproate; 3, octyl aldehyde; 4, dodecane; 5, octanol; 6, tridecane; 7, naphthalene; 8, nitrobenzene; 9, tetradecane; 10, pentadecane; 11, octanoic acid. Conditions: 80 °C for 3 min, 10 °C/min to 130 °C on 10-m BeMIM-TfO column. (B) Separation of homologous series straight-chained alkanes: 1, CH₂Cl₂; 2, octane; 3, nonane; 4, decane; 5, undecane; 6, dodecane; 7, tridecane; 8, tetradecane; 9, pentadecane; 10, hexadecane; 11, heptadecane; 12, octadecane; 13, nonadecane. Conditions: 60 °C for 2 min, 15 °C/min to 180 °C on 10-m BeMIM-TfO column.

that the alkanes interact primarily via dispersion interactions whereas the polar molecules interact via a combination of interactions (i.e., hydrogen bond basicity, π - π , and dipolar). Nevertheless, the IL stationary phases act as excellent nonpolar stationary phases for the separation of a homologous series of straight-chained alkanes, as demonstrated in Figure 3B.

The retention behavior for nearly every alcohol examined in this work was very similar for both the BeMIM-TfO and MPMIM-TfO stationary phases (see Table 4 and Supporting Information). This further supports the idea that the anion, acting as a hydrogen bond base, plays a more significant role in retaining alcohols. Figure 2 in Supporting Information shows the separation of isomeric alcohols on the BeMIM-TfO stationary phase as well as on the DB-17 stationary phase. Interestingly, a reversal of elution order was observed on the IL column indicating that, for this class of molecules, the IL stationary phases display unique selectivity. In addition, the IL column provided more selectivity than the commercial column as seen by the presence of the impurity of 1-chloro-2-propanol (small peak between peaks 4 and 5) in the IL column and the coelution of this peak with peak 2 in the optimized DB-17 separation.

Retention factors for isomeric sulfoxides and isomeric PCBs are also shown in Table 4. Clearly, the size and position of the halogen substituent has a direct influence on the solute retention time. As panels A and B of Figure 4 illustrate using the BeMIM-TfO and DB-17 stationary phases, isomeric sulfoxides with smaller substituents (e.g., fluorine) generally exhibited smaller retention

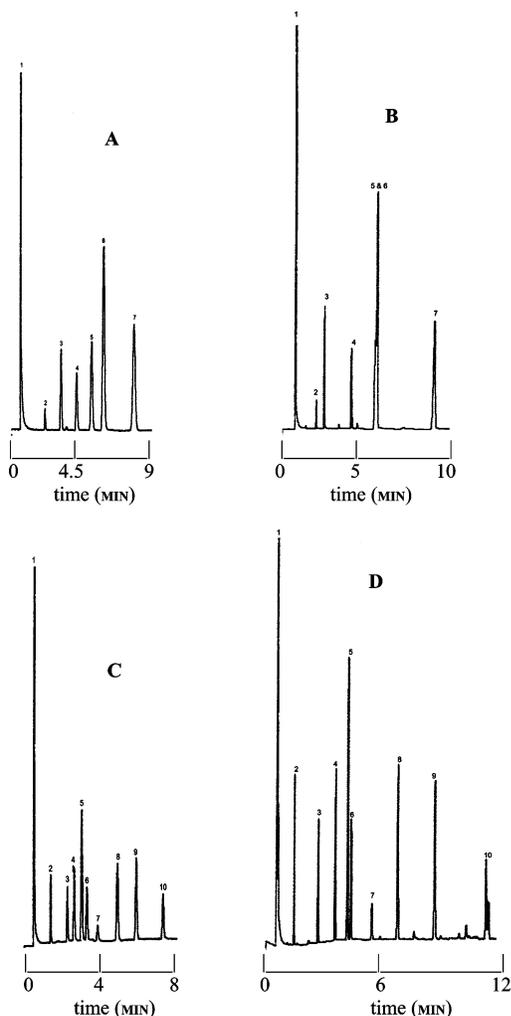


Figure 4. (A, B) Separation of isomeric sulfoxides on (A) 10-m BeMIM-TfO column and (B) 10-m DB-17 column. 1, CH₂Cl₂; 2, *p*-trifluoromethyl methylphenyl sulfoxide; 3, *p*-fluoro methylphenyl sulfoxide; 4, *o*-chloro methylphenyl sulfoxide; 5, *m*-chloro methylphenyl sulfoxide; 6, *p*-chloro methylphenyl sulfoxide; 7, *m*-bromo methylphenyl sulfoxide. Conditions: (A) 170 and (B) 145 °C. (C, D) Separation of PCBs on (C) 10-m MPMIM-TfO column and (D) 10-m DB-17 commercial column: 1; hexane, 2; biphenyl, 3; 3-chlorobiphenyl, 4; 2,2'-dichlorobiphenyl, 5; 2,3'-dichlorobiphenyl, 6; 2,4'-dichlorobiphenyl, 7; 2,2',6-trichlorobiphenyl, 8; 2,2',3-trichlorobiphenyl, 9; 2,2',4,4'-tetrachlorobiphenyl, 10; 2,2',4,4',6,6'-hexachlorobiphenyl. Conditions: 155 °C for 3 min, 3 °C/min to 200 °C.

factors while sulfoxides with bulkier substituents were retained longer. The IL column provided separation of each analyte while the DB-17 stationary phase, under optimized conditions, exhibited coelution of the *m*- and *p*-chloromethylphenyl sulfoxides. In panels C and D of Figure 4, a comparison can be seen between the MPMIM-TfO stationary phase and DB-17 stationary phase in the separation of isomeric PCBs. The IL column is able to provide separation of all nine analytes in under 8 min where the commercial column requires nearly 12 min.

As indicated above, the IL stationary phases are particularly well suited for the separation of isomeric compounds. Figure 5A illustrates the separation of PAHs obtained on the MPMIM-TfO stationary phase. This stationary phase easily resolves the isomers of acenaphthylene and acenaphthene (peaks 4 and 5), fluoranthene and pyrene (peaks 8 and 9), and benzo[*e*]pyrene and benzo[*a*]-

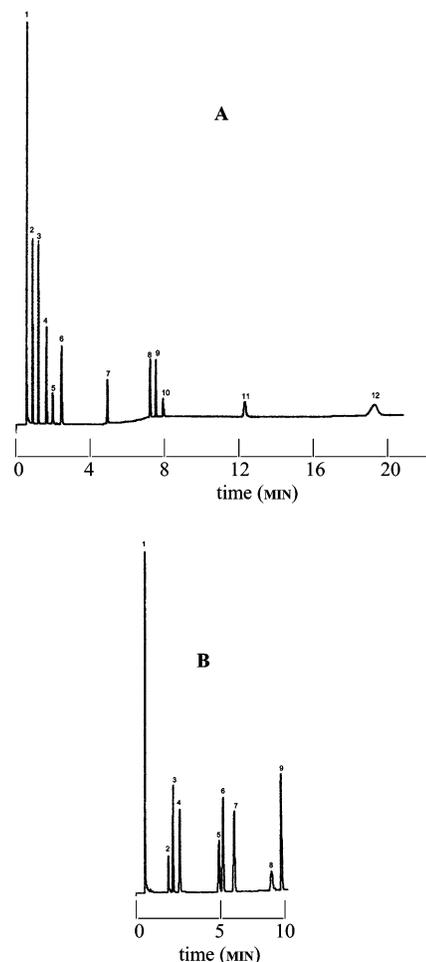


Figure 5. (A) Separation of polycyclic aromatic hydrocarbons: 1, CH₂Cl₂; 2, biphenyl, 3, naphthalene; 4, acenaphthylene; 5, acenaphthene; 6, fluorene; 7, anthracene; 8, fluoranthene; 9, pyrene; 10, 1,2-benzanthracene; 11, benzo[*e*]pyrene; 12, benzo[*a*]pyrene. Conditions: 165 °C for 3 min, 15 °C/min to 230 °C on 10-m MPMIM-TfO column. (B) Separation of chlorinated pesticides: 1, CH₂Cl₂; 2, α -BHC; 3, heptachlor; 4, β -BHC; 5, endosulfan; 6, DDE; 7, dieldrin; 8, endrin; 9, DDT. Conditions: 190 °C on 10-m MPMIM-TfO column.

pyrene (peaks 11 and 12), which are generally difficult to resolve on most commercial stationary phases. Retention factors for two representative PAHs are shown in Table 4. The PAHs are observed to retain considerably longer on the MPMIM-TfO stationary phase. PAHs are capable of interacting with the stationary phase through dispersion forces (*I* interaction parameter) and, more importantly, by π - π interactions (*r* interaction parameter). By comparing the two "*r*" interaction parameters in Table 1, it is clear that the MPMIM-TfO IL is much more capable of undergoing π - π type interactions. Finally, Figure 5B illustrates the efficient, 10-min separation of chlorinated pesticides on the MPMIM-TfO stationary phase. As shown in Table 4 and Supporting Information, the chlorinated pesticides evaluated in this study possessed similar retention behavior.

CONCLUSIONS

Although ionic liquids have many applications in organic synthesis, their usefulness in analytical separations should not be overlooked. They possess many favorable properties that make them unique stationary phases in gas-liquid chromatography.

However, many traditional IL stationary phases have low maximum operating temperatures, produce low peak efficiencies for certain analytes, and strongly retained certain classes of molecules.

Two new ionic liquids based on bulkier imidazolium cations and triflate anions have been introduced to overcome these limitations. The new ionic liquids possess higher bleed temperatures (~ 250 °C), provide symmetrical peak shapes, and still retain the dual-nature retention behavior seen for more traditional ionic liquid GLC stationary phases. In addition, the IL stationary phases provided different elution order for many analytes compared to commercial GC stationary phases. To explain the difference in solvation characteristics for certain analytes, the solvation parameter model was employed to characterize the new ionic liquids. The results indicated that the MPMIM-TfO ionic liquid is able to undergo stronger π - π type interactions than the BeMIM-TfO ionic liquid. These two new stationary phases were shown to produce faster separations of complex mixtures of molecules and often with a selectivity different from commercial GLC stationary

phases. This difference in selectivity is due to the unique solvation characteristics of the ionic liquids and makes them very useful as dual-nature GLC stationary phases. The IL stationary phases are able to separate both polar and nonpolar molecules. Given the favorable characteristics of specific RTILs, they may well be considered a viable class of GLC stationary phases.

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SUPPORTING INFORMATION AVAILABLE

Additional information as noted in text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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